

# PATENT ABSTRACTS OF JAPAN

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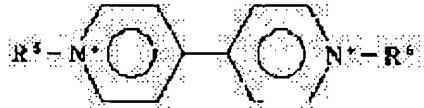
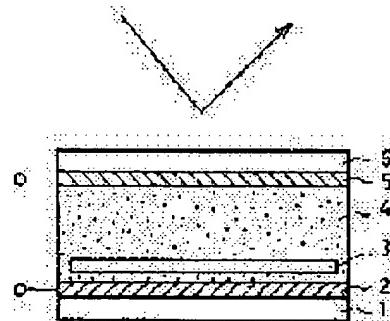
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## (54) ELECTROLYTE SOLUTION FOR ELECTROCHROMIC ELEMENT

### (57)Abstract:

**PURPOSE:** To use excellent electrochromic(EC) coloring characteristics of a viologen deriv. and to obtain an electrolyte soln. for an EC element having low voltage driving property and low haze by dissolving a specified viologen deriv. in a solvent containing a specified alcohol.

**CONSTITUTION:** N,N'-substd.4,4'-bipyridyl (viologen deriv.) expressed by formula II is dissolved in a solvent containing at least one kind of alcohol expressed by HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>R<sub>3</sub>, wherein R is a lower alkyl group and n is an integer 1 to 3. In formula, R<sub>5</sub> and R<sub>6</sub> are independently selected from groups containing aliphatic hydrocarbon or aromatic hydrocarbon. As for the EC display element, for example, it has a laminated structure comprising, from the bottom, glass layer 1, counter electrode 2, back plate 3, solid electrolyte film 4, transparent conductive film 5 and glass plate 6. The solid electrolyte film 4 is produced by impregnating pores of a polymer porous film with the electrolyte soln. above described.



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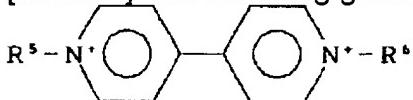
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**CLAIMS****[Claim(s)]**

**[Claim 1]** The following general formula. [Formula 1]



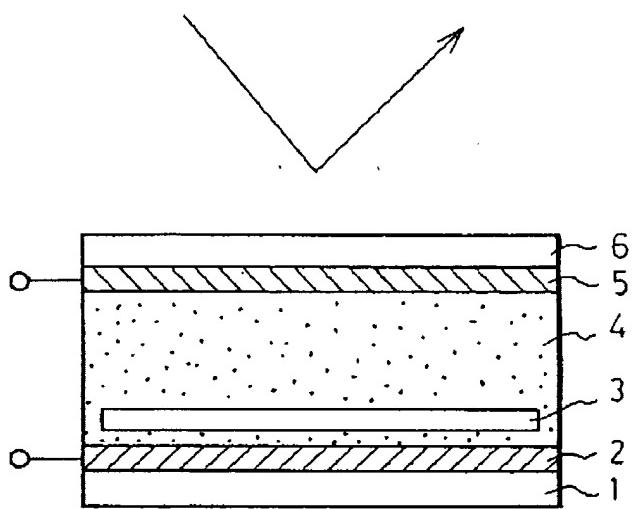
the inside of a formula, R5, and R6 -- respectively -- becoming independent -- an aliphatic system hydrocarbon content machine -- it is chosen out of an aromatic system hydrocarbon content machine It is general formula HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>R3 about the N and N'-substitution 4 expressed and a 4'-bipyridyl (viologen derivative). Inside of [formula, R3 A low-grade alkyl group and n are an electrolytic solution for electrochromic elements characterized by making it dissolve into the solvent containing at least one sort of alcohol expressed with] which is the integer of 1-3.

**[Claim 2]** The electrolyte thin film for electrochromic elements which carries out sinking-in fixation of the electrolytic solution which dissolved N according to claim 1, the N'-substitution 4, and the 4'-bipyridyl in the mixed solvent with a solvent with a refractive index higher than at least one sort of alcohol and the alcohol concerned according to claim 1 at a porosity thin film, and is characterized by the bird clapper.

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Drawing selection [Representative drawing] 

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the electrolyte for electrochromic elements.

[0002]

[Description of the Prior Art] The interest is increasing in the element adapting the electrochromic (EC) phenomenon in which the color of the matter changes with voltage in reversible. An electrochromic element (ECD) has the features, like there is memory nature in which a bright legible large area display is possible (there is little power consumption), and has modulated light elements, such as the large-sized plotting boards, such as a stock price display, a message board, and a guide plate, and an anti-dazzle mirror of an automobile, modulated light glass (aperture), and sunglasses, as application in which such a feature was harnessed.

[0003] The typical structure of ECD is WO<sub>3</sub>, when an electrolyte is arranged, it changes between an electrochromic electrode (WO<sub>3</sub>) and a counter electrode and voltage is impressed between two electrodes. By the electron from the ion and power supply from an electrolyte, cathodic reduction is carried out and it colors.

[0004] Although the solution system of a viologen is studied as the above-mentioned liquid electrolyte, a viologen derivative is further dissolved in the solid polymer electrolyte of a polyethylene oxide, and it is indicated that what sandwiched this between the working electrode and the counter electrode can be used as ECD.

[0005]

[Problem(s) to be Solved by the Invention] In using the solution system of a viologen as an electrolyte like the above ECD which is not suitable for the applied voltage of 2-3V because of a solution system (electrolysis of water occurs), dissolves a viologen derivative in a polyethylene-oxide solid polymer electrolyte on the other hand, and changes Since the macromolecule solid-state polyethylene oxide was used, film intensity was low, large-area-izing was difficult, and also operating voltage was as high as more than 10V, and since it is manufacturing by heat or photopolymerization, after constructing a device, the reaction advanced a little and there were problems -- it is easy to become the cause of degradation.

[0006]

[Means for Solving the Problem] this invention is the (1) following general formula (I), in order to attain the above-mentioned purpose.

[0007]

[Formula 2]



[0008] (-- R5 and R6 are chosen independently from an aliphatic system hydrocarbon content machine and an aromatic system hydrocarbon content machine among a formula, respectively the N and N'-substitution 4 expressed with), and a 4'-bipyridyl (viologen derivative) -- general formula HO (CH<sub>2</sub> CH<sub>2</sub> O)<sub>n</sub> R<sub>3</sub> R<sub>3</sub> is a low-grade alkyl group among [formula, and n is the integer of 1-3. ] The

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electrolytic solution for electrochromic elements characterized by making it dissolve into the solvent which comes out and contains at least one sort of alcohol expressed, And N given in (2) aforementioned (1) term, the N'-substitution 4, and a 4'-bipyridyl The electrolyte thin film for electrochromic elements which carries out sinking-in fixation of the electrolytic solution dissolved in the solvent with a refractive index higher than alcohol and the alcohol concerned given [ aforementioned ] in (1) term at a porosity thin film, and is characterized by the bird clapper is offered.

[0009] It is as follows when the desirable embodiments of this invention are enumerated.

(3) R3 of solvent alcohol Hydrogen or C1 -C4 (1) term which is a straight chain alkyl group, or electrolyte for electrochromic elements given in (2) terms.

(4) (1) term whose solvent alcohol is a 2-methoxyethanol and the 2-ethoxyethanol (R3 is a methyl or ethyl and is n= 1), or the electrolyte for electrochromic elements given in (2) terms.

[0010] (5) the inside R5 of a formula (I), and R6 R5 =R6 it is -- (1) term or electrolyte for electrochromic elements given in (4) terms

(6) the inside R5 of a formula (I), and R6 R5 =R6 it is -- (1) term which is the alkyl group of the shape of a straight chain of the carbon atomic numbers 1-8, and the letter of branching, or electrolyte for electrochromic elements given in (4) terms

(7) The inside of a formula (I), R5, and R6 (1) term which is a heptyl machine, or electrolyte for electrochromic elements given in (4) terms.

[0011] (8) the inside R5 of a formula (I), and R6 R5 =R6 it is -- a phenyl group -- a benzyl -- or -- these -- a basis -- being arbitrary -- a position -- a halogen -- an atom -- a cyano group -- or -- carbon -- an atomic number -- one -- four -- an alkyl group -- replacing -- having -- \*\*\*\* -- a basis -- it is -- (- - one --) -- a term -- or -- ( -- four --) -- a term -- a

(9) the inside R5 of a formula (I), and R6 R5 =R6 it is -- (1) term which are a phenyl group, a benzyl, and 4-cyano phenyl group, or electrolyte for electrochromic elements given in (4) terms

[0012] (10) (1) term whose addition of the viologen derivative of a formula (I) is 1 - 35 % of the weight, or the electrolyte for electrochromic elements given in (9) terms.

(11) (1) term whose addition of the viologen derivative of a formula (I) is 4 - 30 % of the weight, or the electrolyte for electrochromic elements given in (9) terms.

(12) The aforementioned (1) term characterized by including an electrophilic reagent, or the electrolyte for electrochromic elements given in (11) terms.

(13) The electrolyte for electrochromic elements given in (12) terms the aforementioned given electrophilic reagent is a Lewis acid.

(14) The electrolyte for electrochromic elements given in (12) terms the aforementioned given electrophilic reagent is the FURENSUNEDDO acid of proton discharge nature.

(15) The electrolyte for electrochromic elements given in (12) terms with which the electrophilic reagent was chosen from the nitric acid, the hydrochloric acid, and the sulfuric acid.

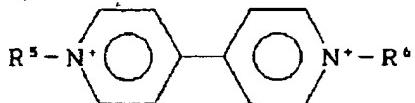
(16) The electrolyte for electrochromic elements given in (12) terms with which an electrophilic reagent is characterized by being a nitric acid.

When an electrochromic element is constituted using such an electrolytic solution, the drive by the about [ 2.5V ] low battery is attained, it excels also in a cycle property, with the coloring property held which was excellent in the viologen derivative, and latus permeability change (7 - 80%) is also attained. even if such an effect can be dealt with as a solid-state, therefore is easy to handle and breaks though it is a solution system when carrying out sinking-in fixation into a stable solid-state porosity thin film although it can demonstrate when using an electrolytic solution as a solution as it is, it can suppress problems, like a solution scatters, and by the large area, a uniform gap acquires it -- having -- liquid -- the seal breakage by whom can suppress

[0013] A viologen derivative is a derivative of a 4 and 4'-bipyridine, and it is the oxidation reduction type compound [ colorlessness ] in which an oxidation type is shown and which a reduction type shows blue - purple, and is expressed with the following general formula.

[0014]

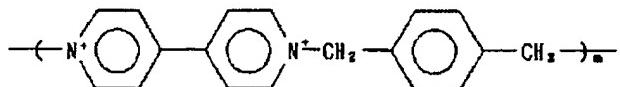
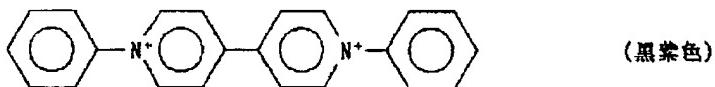
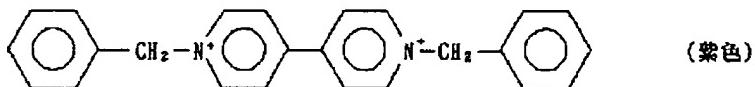
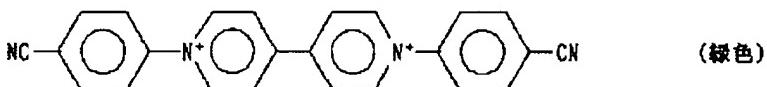
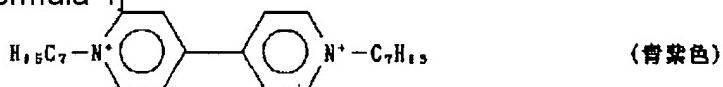
[Formula 3]



[0015] The inside of the above-mentioned formula, R5, and R6 It is R5 although chosen from the basis chosen independently from an aliphatic system hydrocarbon content machine or an aromatic system hydrocarbon content machine, respectively. R6 The same thing is desirable. as an aliphatic system hydrocarbon content machine -- desirable -- the alkyl group of the shape of a straight chain, and the letter of branching -- more -- desirable -- the alkyl group of the shape of a straight chain of the carbon atomic numbers 1-8, and the letter of branching -- it is n-heptyl machine especially or the basis by which the arbitrary positions of a phenyl group, benzyls, or these bases are replaced as an aromatic system hydrocarbon content machine by the halogen atom, the cyano group, or the alkyl group of the carbon atomic numbers 1-4 -- they are a phenyl group, a benzyl, and 4-cyano phenyl group more preferably More specifically, methylation, the benzyl-ized derivative, and the following compound are illustrated in a 4 and 4'-bipyridine. This viologen derivative has the advantage which can realize multiple color by choosing the kind of derivative.

[0016]

[Formula 4]



[0017] Such a viologen derivative is general formula HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>R<sub>3</sub>. It dissolves in the solvent which consists of at least one sort of alcohol expressed with [a low-grade alkyl group and n of the inside of a formula and R<sub>3</sub> are the integers of 1-3].

[0018] a desirable solvent -- the inside of the above-mentioned formula, and R<sub>3</sub> hydrogen or the alcohol of a straight chain-like lower alcohol (especially carbon atomic numbers 1-4) -- further -- desirable -- R<sub>3</sub> It is the 2-methoxyethanol and 2-ethoxyethanol which are a methyl or ethyl and are n=1.

[0019] The addition of the viologen derivative to the inside of the above-mentioned solvent is 5 - 30 % of the weight more preferably one to 35% of the weight. When fewer than 1 % of the weight, there is a fault in which the permeability by the side of the coloring when wearing and performing decolorization operation does not fully fall, when [ than 35 % of the weight ] more, it is hard to solve in a solvent, and there is a fault which is moreover easy to carry out the color remainder. the permeability when wearing 5 - 30% of the weight of a case, and performing decolorization operation -- 10% or less --

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becoming -- the solubility of a viologen derivative -- eye a good hatchet -- it is the most desirable [0020] At this invention, it is general formula HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>R<sub>3</sub> about the N and N'-substitution 4 and a 4'-bipyridyl. The inside R<sub>3</sub> of [formula is a low-grade alkyl group, and n is the integer of 1-3.] By coming out and making it dissolve in a solvent at least with a refractive index higher than a kind of alcohol expressed and the alcohol concerned, like JP,3-67227,A, it can be filled up during hole of a solid-state macromolecule porosity thin film, and an electrolyte thin film can be constituted. This mixed solvent has a refractive index from 1.45 to 1.53, and since it is close to 1.49-1.53 which are the general refractive index of a macromolecule porosity thin film, it is effective in reducing the rate of haze of the thin film after sinking-in fixation. General formula HO (CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>R<sub>3</sub> The inside R<sub>3</sub> of [formula is a low-grade alkyl group, and n is the integer of 1-3.] If a refractive index is higher than the alcohol concerned, although especially a kind will not be asked as a solvent out of which it comes and which is mixed with the alcohol expressed, aromatic nitril, for example, a diphenyl propionitrile etc., is raised. This electrolyte thin film holds the intensity of a solid-state macromolecule porosity thin film, and thin-film-izing and large-area-izing are possible for it. For 0.1 micrometers - 50 micrometers and a void content, as a solid-state macromolecule porosity thin film of this invention, 40% - 90% and breaking strength are [ thickness ] 200 kg/cm<sup>2</sup>. That whose diameter of an average breakthrough is 0.01 micrometers - 0.7 micrometers is used preferably above.

[0021] Generally the thickness of a thin film is 0.1 micrometers - 50 micrometers, and is 1.0 micrometers - 25 micrometers preferably. It is difficult for thickness to present practical use in less than 0.1 micrometers from the fall of the mechanical strength as a supporting lamella, and the field of handling nature. It is not desirable from a viewpoint of on the other hand stopping effective resistance low when exceeding 50 micrometers. It is 60% - 90% of range often [ the void content of a porous thin film / considering as 40% - 90% ], and preferably. When a void content becomes insufficient [ less than 40% / the ion conductivity as an electrolyte ] and exceeds 90% on the other hand, it is difficult for the mechanical strength as a supporting lamella to become small, and to present practical use.

[0022] Although the diameter of an average breakthrough just fixes an ionic conductor during hole, generally it is 0.01 micrometers - 0.7 micrometers. The desirable diameter of an average breakthrough is based also on the quality of the material of a poly membrane, or the configuration of a hole. Generally the breaking strength of a poly membrane is 200 kg/cm<sup>2</sup>. They are 500 kg/cm<sup>2</sup> more preferably above. It is suitable for the utilization as a supporting lamella by having the above. The porous thin film used for this invention has a function as a base material of the above ionic conductors, and consists of polymeric materials which were excellent in the mechanical strength.

[0023] Although a polyolefine, a polytetrafluoroethylene, and a polyvinylidene fluoride can be used from a viewpoint of chemical stability, for example, especially for one example of suitable polymeric materials, weight average molecular weight is 5x10<sup>5</sup> from a viewpoint of the ease of coexistence of the design, thin-film-izing, and the mechanical strength of the porous structure of this invention. It is the above polyolefine. namely, the crystalline line of the homopolymer of an olefin, or a copolymer -- a polyolefine -- the weight average molecular weight -- 5x10<sup>5</sup> the above -- desirable -- 1x10<sup>6</sup> to 1x10<sup>7</sup> It is a thing. For example, polyethylene, polypropylene, an ethylene propylene rubber, polybdenum -1, the poly 4-methyl pentene -1, etc. are raised. Among these, weight average molecular weight is 5x10<sup>5</sup>. The above polyethylene or polypropylene is desirable. The weight average molecular weight of a polyolefine influences the mechanical strength of the transparency film obtained. By super-drawing, the amount polyolefine of super-macromolecules is ultra-thin, enables film production of high intensity, and is taken as the base material of the low high ion conductivity thin film of effective resistance. Weight average molecular weight is 5x10<sup>5</sup>. Although the polyolefine of the following can be used simultaneously, weight average molecular weight is 5x10<sup>5</sup>. By the system which does not contain the above polyolefine, the film of the ultra-thin high intensity by super-drawing is not obtained.

[0024] The above porous thin films can be manufactured by the following methods. Into a solvent like a liquid paraffin, the heating dissolution of 1 % of the weight - the 15 % of the weight is carried out, and let the amount polyolefine of super-macromolecules be a uniform solution. A sheet is formed from this solution, and it quenches and considers as a gel sheet. Extraction processing is carried out with a volatile solvent like a methylene chloride, and the amount of solvents contained in this gel

sheet is made into 10 % of the weight - 90 % of the weight. This gel sheet is heated at the temperature below the melting point of a polyolefine, and it extends to 10 or more times for a field scale factor. The solvent contained in this extension film is dried after carrying out extraction removal with a volatile solvent like a methylene chloride.

[0025] The example of another suitable polymeric materials is a polycarbonate, and the solid-state macromolecule porosity thin film in this case irradiates a charged particle all over a reactor to a polycarbonate thin film, and can also be produced by the method of carrying out alkali etching of the track which the charged particle passed, and forming a hole. As for such a thin film, Kamiichi of a polycarbonate and the polyester product is carried out as for example, a new chestnut pore membrane.

[0026] In addition, polyester, poly methacrylate, a polyacetal, a polyvinylidene chloride, tetrafluoro polyethylene, etc. can be used. As a method filled up with an ionic conductor into a macromolecule thin film \*\* The viologen derivative dissolved in the solvent, or the viologen derivative made [ the shape of a sol and the gel] to carry out differential powder into a solvent [ whether a solid-state macromolecule porosity thin film is infiltrated and ] By the manufacturing process of \*\* porosity thin film which removes a solvent an application or after carrying out a spray, the solution of a viologen derivative Or the method of \*\* which the monomer and fusibility precursor of \*\* viologen derivative which produce a film after mixing the sol or the distributed solution of a gel are infiltrated into a solid-state macromolecule porosity thin film, or is made to react within hole an application or after carrying out a spray can be used.

[0027] In order to constitute ECD using the electrolyte thin film like the above, an electrolyte thin film is inserted by the transparent electric conduction electrode and the counter electrode. There are SnO<sub>2</sub>, ITO, etc. as a transparent electric conduction electrode, and a counter electrode can use the matter colorless by both electrode or oxidation-reduction reactions that carry out oxidization coloring, such as NiO, IrO<sub>x</sub>, and a Prussian blue, etc. If a viologen derivative receives electron from an ITO electrode, it will be returned and will color. At this time, since ITO will be returned if not much high voltage is impressed, less than [ 3V ] is desirable.

[0028] The example of production of an electrochromic element is explained using a drawing. The example of EC display device is shown in drawing 1. In this laminated structure, they are the lower shell glass plate 1, a counter electrode 2, the background board 3, the solid electrolyte film 4, the transparent electric conduction film 5, and a glass plate 6. Since this display device is reflective mode, a glass plate 1 does not necessarily need to be a transparent board, and a resin board etc. is sufficient as it. A counter electrode 2 has little generating of hydrogen or oxygen, and electronic conductivity material with large electric capacity with sufficient reversibility is used to an electrochemical oxidation-reduction reaction. Specifically, there is a composite of carbon, and transition metals and carbon etc. The thickness of a counter electrode 2 is about 0.1-10 micrometers.

[0029] The background board 3 has a common white background board, for example, the sheet which kneaded and fabricated alumina powder with the binder can be used. The background board 3 can also be served by the counter electrode 2. The solid electrolyte film 4 sinks in the electrolytic solution which dissolved an aforementioned specific solvent and an aforementioned viologen compound during hole of for example, a macromolecule porous membrane, and thickness is the solid electrolyte film which has the ion conductivity of 4-20 micrometers and  $1.5 - 2.5 \times 10^{-4} \text{ S/cm}$ .

[0030] The transparent electric conduction film 5 is a collector, and it is indium-tin-oxide (ITO) tin oxide etc., and thickness is 0.1-0.2 micrometers and is formed on a glass plate 6. The voltage impressed between the transparent electric conduction film 5 and a counter electrode 2 is good about 2.5V. Since ITO will be returned if not much high voltage is impressed at this time, it is not desirable. In this way, since the electrolyte is fixed in the poly membrane, EC element created can be substantially dealt with as a solid-state film and there are no worries about a liquid spill even if structure is easy and it moreover assembles, and the handling at the time is also easy and damages after assembly, special cautions are unnecessary like [ in the case of a liquid electrolyte ].

[0031] the point that the structure of drawing 2 differs from drawing 1 -- as a counter electrode 13 -- like \*\*\*\* -- IrO<sub>x</sub> etc. -- it uses, is formed by the thickness of 0.05-0.2 micrometers, and is the point which is light-transmission nature

[0032] With the structure of drawing 1, the background board 3 may be light impermeability nature, and the light impermeability nature of a counter electrode 2 may also be permeability. With the structure of drawing 2, it acts as modulated light glass (EC window) by impressing voltage by making the electric conduction film 15 into negative voltage between the electric conduction film 12 and 15. In addition, if a counter electrode 13 is patternized with this structure, it can be used also as a penetrated type display device.

[0033]

[Example]

(1) Manufacture 2-methoxyethanol 10g of a solution was taken, and best nitric-acid 0.1wt% was added heptyl viologen 10wt%. Stirring mixture was improved in the beaker using the stirrer.

[0034] (2) The spacer was intervened between 40mm (A, B) angles of element manufacture (anti-dazzle mirror) \*\* two glass substrates (interval of 20 micrometers), and the seal of the surrounding seal was carried out using ultraviolet-rays adhesives. The inlet of one place and a solution was opened at this time. However, glass-substrate A is ITO/glass substrate, and glass-substrate B attached \*\*\*\* to the rear face of ITO/glass substrate.

\*\* The electrolytic solution was poured in. The whole is lengthened to about 500Pa or less of vacuums by the vacuum chamber, the solution was dipped, and it poured in at the room temperature (22 degrees C).

\*\* The seal of the inlet was again carried out with ultraviolet-rays hardening adhesives after pouring.

[0035] (3) Element drive evaluation initial-current voltage characteristic evaluation was performed. (2 pole type)

Driver voltage is 2.5V and checked visually about the color remainder. A result is shown in a table (example : Table 1, the example of comparison : table 2). In this example, the nitric acid is added for the improvement in a cycle property. It turns out that the element which used the solution which consists of a heptyl viologen and a 2-methoxyethanol, or a 2-ethoxyethanol from this table shows a good electrochromic characteristic.

[0036]

Table 1. Cycle property of EC element (example)

----- example Solvent It operates without carrying out the color remainder.

Nitric-acid concentration The made number of cycles (time) (wt%)

----- 1 2-methoxyethanol 2000-3000 0.1 2 2-ethoxyethanol 700- 800 1.0 -----

----- [0037]

Table 2. Cycle property of EC element (example of comparison)

Example of ----- comparison Solvent It operates without carrying out the color remainder. Nitric-acid concentration The made number of cycles (time) (wt%)

----- 1 Propylene glycol 0 1.0 2 1, 3-butanediol 0 1.0 3 Ethyl phenyl hide light 0

1.0 4 Benzyl alcohol 0 1.0 5 2-phenyl ethanol 200-300 1.0 ----- [0038] (4)

Reflection factor measurement heptyl viologen 10wt% of the electrochromic element, the electrolytic solution which consists of nitric-acid 0.1wt% and a 2-methoxyethanol was injected into EC element (glass / ITO / electrolytic-solution layer / ITO / glass / Ag mirror), and the reflection factor of this element was measured. The relation between driver voltage and a reflection factor is shown in a table.

[0039]

表3. 駆動電圧と反射率の関係

駆動電圧 (V)	反射率 (%)
0	82.3
2.00	35.6
2.25	28.2
2.50	23.4
3.00	15.4

[0040]

[Effect of the Invention] According to this invention, taking advantage of the electrochromic coloring property which was excellent in the viologen derivative, the electrolytic solution for EC elements of a low-battery drive and the rate of low haze is offered. moreover, the thing done for the sinking-in fixation of this electrolytic solution at a solid-state porosity thin film -- the ion conductivity as a liquid electrolyte -- \*\*\*\*\* -- there are nothings and it is possible to deal with it as a solid-state

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